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COMPLETE ANALYSIS OF IONIC STAINING OF GLASSES BY TRANSITION-METAL COMPOUNDS

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The data on the ionic staining of glasses are analyzed from the standpoint of ligand field theory. New information is added to the existing information on the staining of glasses by transition-metal compounds. Data on the structure of glass-forming melts and the conditions for the formation of staining complexes are presented. A possible mechanism for amber staining in glasses is discussed.

Ionic staining of glasses is accomplished, as a rule, with transition and rare-earth elements. Some of these compounds can also be used for decolorize glasses, which is a kind of staining.

The current view is that staining is due to the formation of coordination (complex) compounds in which the character of the chemical bond is studied from the standpoint of the valence-bond, crystal-field, and molecular-orbital theories [1 – 3]. The basic tenets of these theories as applied to the transition elements are gathered under the name “ligand field theory.” The methods used in this theory make it possible to calculate quite accurately the spectral characteristics of coloring complexes, including for glasses [1, 3 – 5].

The present article presents a complete analysis of ionic staining of glasses. The relationship between color centers and the basic structural elements of glasses is very important for glass technology. This relationship is quite complicated and can be viewed, for example, from the standpoint of the

solvation interaction, whose basic ideas as applied to solutions are developed in the monograph [6] and have essentially not been studied for glasses.

Ligand field theory studies the interaction of ligands on the d or f orbitals of a complexing ion. Ligands split the corresponding energy levels of the orbitals.

The present article will focus on ionic staining determined by the $3d$ orbitals of ions of transition elements and oxygen ligands. In addition, the mechanism proposed for the formation of complexes with mixed ligands will be examined for the example of amber staining of glass.

Ionic staining of glass by transition-metal compounds, as a rule, is associated with octahedral and tetrahedral arrangements of ligands around a complexing ion. The form and spatial arrangement of the d orbitals and their energy levels in the octahedral and tetrahedral environment of ligands (for one spatial variant) are displayed in Fig. 1. In an octahedral ligand field three electron orbitals occupy the lowest energy level d_e while two orbitals occupy the higher energy level d_g . The opposite picture is observed in a tetrahedral ligand field. When studying transition elements with an increasing num-

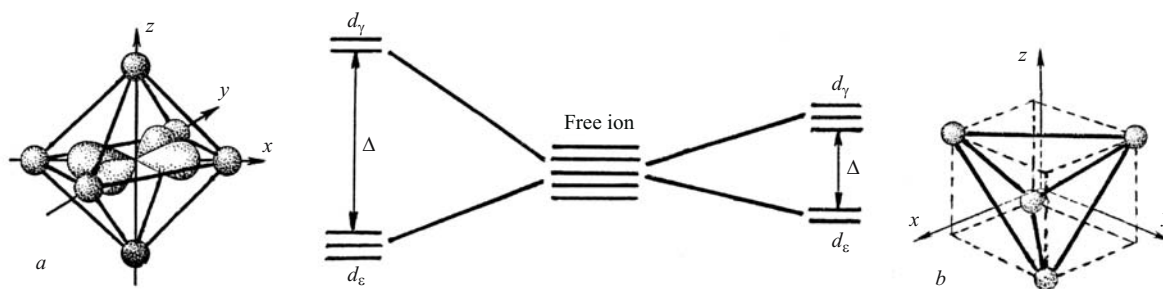


Fig. 1. Splitting of the energy levels of d electrons in octahedral (a) and tetrahedral (b) fields of oxygen ligands.

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TABLE 1.

Metal ion	Electronic configuration	Coordination	<i>d</i> Orbital splitting, cm^{-1}	Orbital configurations	Electron arrangement*		Complex ion	Hybridization	Optical characteristics		
					d_ϵ	d_γ			glass color	color intensity	absorbed region of the spectrum
Cr^{6+}	$3d^0$	4		d^0			$[\text{CrO}_4]^{2-}$	sd^3	Yellow. Intense absorption in the UV region	Average	Short-wavelength, including UV
Ti^{3+}	$3d^1$	6	18,200	d_ϵ^1			$[\text{TiO}_6]^{3-}$	d^2sp^3	Colorless. Intense absorption in the UV region		
V^{3+}	$3d^2$	6	15,800	d_ϵ^2	$\uparrow\uparrow$		$[\text{VO}_6]^{3-}$	d^2sp^3	Colorless or greenish. Absorption in the UV region	Very low	
Cr^{3+}	$3d^3$	6	15,500	d_ϵ^3	$\uparrow\uparrow\uparrow$		$[\text{CrO}_6]^{3-}$	d^2sp^3	Green	High	
Mn^{3+}	$3d^4$	6**	18,700	$d_\epsilon^3d_\gamma^1$	$\uparrow\uparrow\uparrow$	\uparrow	$[\text{MnO}_6]^{3-}$	d^2sp^3	Violet. Absorption in the UV region	Average	
Mn^{2+}	$3d^5$	4	3100	$d_\epsilon^3d_\gamma^2$	$\uparrow\uparrow\uparrow$	$\uparrow\uparrow$	$[\text{MnO}_4]^{2-}$	sp^3	Colorless or yellowish	Very low	
Fe^{3+}	$3d^5$	6	12,200	$d_\epsilon^3d_\gamma^2$	$\uparrow\uparrow\uparrow$	$\uparrow\uparrow$	$[\text{FeO}_6]^{3-}$	d^2sp^3	Yellow-green. Absorption in the UV region	Low	
Fe^{2+}	$3d^6$	6	9300	$d_\epsilon^4d_\gamma^2$	$\downarrow\uparrow\uparrow\uparrow$	$\uparrow\uparrow$	$[\text{FeO}_6]^{4-}$	d^2sp^3	Blue-green. Absorption in the IR region	Average	Long-wavelength, including IR
Co^{2+}	$3d^7$	4	3700	$d_\epsilon^3d_\gamma^4$	$\uparrow\uparrow\uparrow$	$\uparrow\downarrow\uparrow\downarrow$	$[\text{CoO}_4]^{2-}$	sp^3	Dark blue. Absorption in the IR region	Very high	
Ni^{2+}	$3d^8$	4	3400	$d_\epsilon^4d_\gamma^4$	$\uparrow\uparrow\downarrow\uparrow$	$\uparrow\downarrow\uparrow\downarrow$	$[\text{NiO}_4]^{2-}$	sp^3	Yellow-brown. Absorption in the IR region	High	
Cu^{2+}	$3d^9$	6**	11,200	$d_\epsilon^5d_\gamma^4$	$\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow$	$\uparrow\downarrow\uparrow$	$[\text{CuO}_6]^{2-}$	d^2sp^3	Light blue. Absorption in the IR region	Average	

* $\uparrow\downarrow$) unpaired electrons, $\uparrow\downarrow$) paired electrons.

** Tetragonal distortion — Jahn – Teller effect.

ber of $3d$ electrons the successive filling rule must be followed, starting with low-energy orbitals.

The splitting Δ depends on the nature of the ligands and the configuration of the complex. If the ligands and their distances from the complexing center are the same, then Δ for a tetrahedral environment is approximately 4/9 times its value for an octahedral environment. The splitting Δ can be calculated by the theoretical methods of quantum mechanics and determined on the basis of experimental data on the absorption spectra of complex compounds [1 – 5].

The optical absorption spectra in the visible, ultraviolet, and near-infrared regions are due to radiative transitions of electrons from certain energy levels to other energy levels. The basic tenets of quantum mechanics prohibit certain electronic transitions in accordance with the quantum numbers of the orbitals (Laporte selection rules) and the change in the number of unpaired electrons (selection according to spin). These prohibitions lower the intensity of $d-d$ transitions and are “lifted” when a color complex is formed, specifically, when its symmetry is broken (the Jahn – Teller effect), and as a result of charge transfer effects. When examining absorption spectra, especially in the IR region, the interaction of purely electronic transitions with the vibrations of the

structure framework of the glass must be taken into account. It should be noted especially that any absorption band in glass is an electronic – vibrational band.

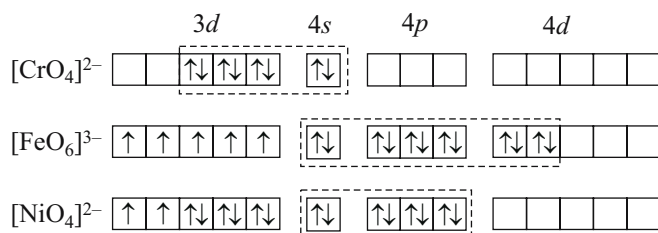
Characteristics of Ionic Staining. The data obtained on the basis of the ligand field theory make it possible to draw definite qualitative conclusions concerning the technological characteristics of stained glasses.

General and supplementary information on the ionic centers of transition elements in glasses are presented in Table 1. It is evident that intracomplex interactions are related with the character of the staining of glass. The absorption bands of transition-metal complexes cover primarily the spectral regions in the wavelength range 200 – 1200 nm and are due mainly to the electronic transitions of the d sphere of the central ion. But, as a rule, the intensity of the absorption bands due to these transitions is much lower than that of the transitions with charge transfer.

The color intensity can be explained from the standpoint of the symmetry of the coordination polyhedra, which is due to the distribution of the electrons over the orbitals. As a rule, octahedral complexes with coordination number (CN) 6 give much weaker color than tetrahedral complexes (CN = 4), even though the splitting of the electronic energy levels is larger. This is due to a change in the symmetry of the com-

plex (an octahedron has a center of symmetry, a tetrahedron does not). It should be noted that a complex particle is capable of existing in a host of almost energy-equivalent configurations. In time a complex “runs through” all of these configurations, and the coordination structures adopted (tetrahedron, octahedron, and others) are averages.

Since in most cases the metal complexing ion can contribute energetically nonequivalent electronic orbitals for bond formation, it is assumed that hybridization of the orbitals, which depends on the electronic structure of the metal ion and on the nature of the ligand, is necessary for bond formation. The character of the hybridization is indicated for the complex transition-metal ions presented in Table 1; it can be clearly reflected in the form of the bonding schemes for electronic orbitals. As an example, such schemes for complex chromium, iron, and nickel ions are presented below.



It follows from these schemes that $[\text{CrO}_4]^{2-}$ is an inner-orbital complex while $[\text{FeO}_6]^{3-}$ and $[\text{NiO}_4]^{2-}$ are outer-orbital complexes.

The absorbed region of the spectrum also is directly related with the electronic interaction in the coloring complex. As a rule, triply charged transition-metal ions have a smaller radius and therefore a stronger force field than doubly charged ions. Their “covalency factor” is also larger [7]. In this case the splitting of the energy levels increases, and for this reason the absorption bands shift into the short-wavelength region of the spectrum. Absorption in the low-energy long-wavelength visible and IR regions of the spectrum is characteristic for doubly charged ions. The absorption level in these regions can characterize the relation between the coloring complex and the main structural elements of the glassy medium (solvation interaction). Both mechanisms are interrelated. For example, for iron complexes a transition from the d^5 to the d^6 electronic configuration weakens the inner-complex bonds, which results in stronger outer bonds. Such bond redistribution can characterize the diathermancy of glasses, which plays a large role in glass making and article formation [8].

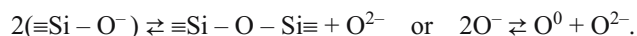
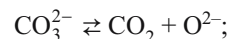
Salient Structural Features of Glass Melts and the Formation of Coloring Complexes. In the simplest case, glass melt forms when solid SiO_2 interacts with molten Na_2CO_3 . Information about the kinetics and mechanism of this process is presented in [9]. Ultimately, the melt obtained is based on silicon – oxygen formations with different degrees of complexity and linkage (network, framework). Alkali-metal ions occupy voids in the structure, decreasing the free volume of the melt and increasing the mobility of the

framework as a whole and of its individual elements, specifically, the small and terminal sections of extended silicon – oxygen formations. In this connection the viscosity decreases and transfer processes are activated. In addition, the activity of the oxygen ions increases. During the making of stained glass the crystal lattice of the coloring compounds (stains, impurities in the initial materials) breaks down and oxygen coordination polyhedra form around the central transition-metal ions. As a rule, this process is accompanied by redox interactions.

In summary, stained glass can be regarded as a solution of complex transition-metal compounds in a glassy medium. In this connection, the interactions occurring in the coloring complex + glassy solvent system will play an important role. As mentioned above, for all practical purposes these interactions have not been studied for glasses. It is obvious that theoretical work and experimental studies in this field are needed.

The coloring processes and the accompanying redox interactions can be characterized by the activity of the oxygen and transition-metal ions.

As a result of chemical reactions and thermal and electrolytic dissociation, three forms of oxygen ions, which are in equilibrium, are present in glass melts. For example, for $\text{Na}_2\text{O} - \text{SiO}_2$ melts we can write



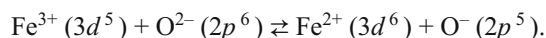
The ratios of the three forms of oxygen ions are determined by the law of mass action, and the equilibrium constant is given by the relation

$$K = \frac{[\text{O}^0][\text{O}^{2-}]}{[\text{O}^-]}.$$

An analysis of the indicated equilibria using the law of mass action is presented in the work of G. W. Toop and C. S. Samis (1962) and is generalized in the monograph [10].

The chemical properties of the three types of oxygen ions are substantially different. The ion O^{2-} acts as a reducing agent (it gives up an electron) and the ion O^- mainly acts as an oxidizing agent (it accepts an electron). The bridging ion O^0 , being covalently bound with silicon ions, is essentially inactive, but it still interacts with some reagents, for example, water.

A characteristic example of the different roles played by oxygen ions is the redox interaction of iron ions in accordance with the electron – ion equation of the reaction (the electronic configuration of the ions is shown in parentheses):



Oxygen ligands which coordinate around a central transition-metal ion are characterized by comparatively small sizes

and weak polarizability, and they have lone-pair electrons. Oxygen ions generate a comparatively weak ligand field, whose strength is comparable to that of the aquocomplexes (approximately 10 – 12% weaker than for H₂O ligands). As a result, the optical characteristics due to electronic transitions are close, which has been confirmed in [4, 5] for binary alkali – silicate and alkali – borate glasses. Information on other types of stained glass and the corresponding ligands is systematized in the monograph [11] with references to the original works.

The activity of transition-metal ions in glass melt with formation of coordination polyhedra is determined by the following:

the nature of the ion (size, charge, electronic configuration, polarizability, and so on);

the type and characteristic of the ligands in the coordination polyhedron;

the coordination number and symmetry of the coordination polyhedron; and,

the temperature conditions.

The table of the electronic characteristics shows that, as a rule, the splitting of the energy levels of the 3*d* orbitals is smaller than for ions with a low charge, Cu²⁺ being an exception. This is because the ions with a high charge interact more strongly with ligands than ions with a low charge, and they form stronger bonds with ligands. The corresponding hybridization and the character of the inner-complex bonds promote this. The chemical interaction between the components of the batch during glass making produces an adequate number of active oxygen ions which participate in the formation of the coloring complexes. Outer-orbital complexes, in which the bonding electronic orbitals are in the outer sphere with completely filled 3*d* orbitals (Mn²⁺, Fe³⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺), form quite rapidly. If the bonds touch the intracomplex 3*d* orbitals, the coloring complexes form more slowly. As a rule, the splitting of their electronic levels is large (Ti³⁺, V³⁺, Cr³⁺, Mn³⁺). A characteristic example is the Cr³⁺ complex, which forms slowly. In addition, chromium compounds have limited solubility in glass.

Mechanism of Formation of Coloring Complexes. Redox Interactions. As mentioned above, coordination polyhedra of transition-metal ions form in glass during founding. The mechanism of this process is quite complicated and has essentially not been studied for glass-forming melts. This is due to experimental difficulties for high-temperature processes and because the theoretical questions concerning the interaction of coloring complexes with a glassy medium have not been adequately analyzed. At the same time substantial theoretical and experimental data on the chemistry of coordination compounds in crystals and solutions have been accumulated [1 – 3, 12]. A number of the results obtained are applicable to stained glass, specifically, for calculating the position and intensity of the absorption bands and using the ligand field theory to explain the results obtained [4, 5, 11].

Viewing stained glasses as solutions containing complex transition-metal ions, a possible mechanism for the forma-

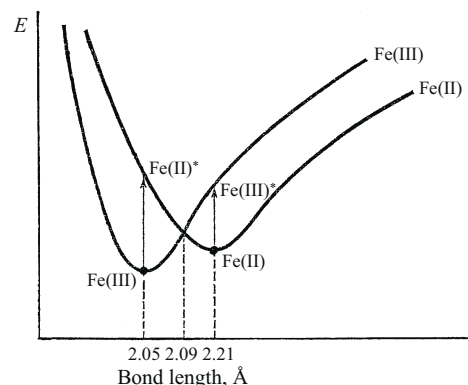
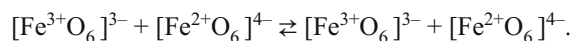


Fig. 2. Diagram of the variation of the potential energy as a function of the Fe – O bond length (Fe(II)* and Fe(III)* — ions in the excited state).

tion of coloring complexes can be proposed on the basis of the modern theory. It should be noted that the microscopic nonuniformity of glass, which is especially pronounced in silicate glass used for hollow glassware (glass containers, dishware, and others), affects the configuration of the coordination polyhedra. When glass is formed from melt, transition-metal ions have more “freedom to choose” a localization site and a configuration for the complex than when a crystal structure is formed. This is explained by the fact that when crystals form, the crystallographic parameters control the interionic distances and the symmetry of the complexes more strictly.

We shall examine first the reversible equilibrium reaction between two iron complexes where the central metal ions have identical coordination shells but different degrees of oxidation:



In such reactions reversible electron transfer does not change the concentration of any reactant and for this reason is not accompanied by a change in the free energy. Electron transfer processes in such reactions must proceed in accordance with the Franck – Condon principle, according to which before electron transfer occurs the reacting compounds must be “reorganized” so that the energy in the transitional state would be the same.

We now present the dependence of the potential energy on the Fe – O bond length (Fig. 2). In ground states the Fe – O bond in the case of Fe²⁺ is longer (2.21 Å) than in the case of Fe³⁺ (2.05 Å). Therefore, in order for electron transfer to be possible the energies of the reacting compounds must be “equalized” as a result of bond compression, stretching, or bending. This is a fundamental principle for any chemical interaction. In addition, the character of the hybridization of the orbitals, rearrangement of the solvation shells, and some other factors make their own contributions.

The character of the hybridization of the orbitals determines the reactivity of the coloring complexes which largely

depends on the rate of exchange, occurring in stained glasses, of the ligands of a complex. Transition-metal complexes are usually divided into labile (high rate) and inert (low rate) on the basis of the ligand exchange rate. The conditions promoting ligand exchange are as follows:

“outer” hybridization;

presence of free inner $3d$ orbitals in a complex.

It should be noted that oxygen complexes of transition-metal ions with the configurations d^4 , d^5 , d^6 , and d^9 are ordinarily labile because of “outer” hybridization while d^0 , d^1 , and d^2 complexes are labile because free $3d$ orbitals are present. Ionic complexes with the configurations d^3 , d^7 , and d^8 are inert. For complexes with an octahedral structure (Cr^{3+}) electrons with parallel spins occupy energetically “more favorable” orbitals d_e , and for complexes with tetrahedral structure (Co^{2+} , Ni^{2+}) electrons with paired spins occupy the energetically “more favorable” orbitals d_t .

In the case of “outer” hybridization the bond between ligands and a complexing ion is weaker than for “inner” hybridization. Consequently, in the presence of an external perturbation (action of oxidizers or reducers) one or more ligands can detach more easily, giving up its place to others (substitution reaction).

An examination of the kinetic characteristics of transition-metal complexes in glasses reveals that dissociative mechanisms of substitution reactions, related with the temporary removal of a replaceable ligand, must correspond to higher activation energies and low rates for the process. Another path for substitution reactions is opened up by associative mechanisms, for which a temporary presence of both ligands (leaving and arriving) in the bound state is characteristic.

The activated complex theory is ordinarily used to explain the mechanism of the interaction with the participation of complex compounds [2, 12]. In a number of cases, near the maximum energies, a metastable particle possessing all properties of an individual chemical substance can exist in the reaction path. Such a particle is usually called an intermediate (intermediate compound). In this case the reaction $A \rightarrow B$ actually reduces to two intermediate reactions: $A \rightarrow C$ and $C \rightarrow B$.

It is of great interest to examine the possible mechanism of the interaction yielding amber color, which is widely used for glass containers (bottles).

As shown in [13, 14], amber color is due to a complex with tetrahedral coordination of Fe^{3+} with three oxygen ions and one S^{2-} ion. The S^{2-} ions can be obtained by introducing either Na_2SO_4 with excess reducing agent or blast-furnace slag containing S^{2-} . The conditions for obtaining amber and brown glasses are examined in [15].

Glass with the commercial composition of bottle glass has been made using blast-furnace slag. Curves of the spectral transmission of these glasses made under various redox conditions are presented in Fig. 3. These conditions are regu-

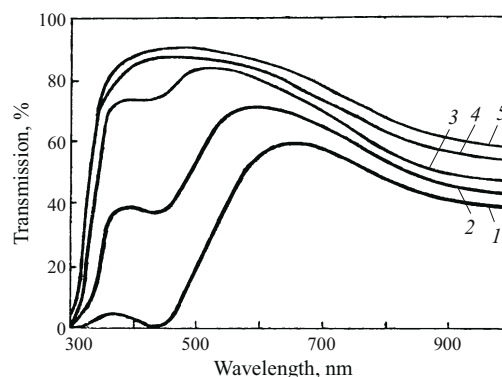


Fig. 3. Spectral transmission curves of glasses made under different redox conditions with added oxidizer: Na_2SO_4 content (% of the slag introduced): 1) 13.6; 2) 18.4; 3) 24.8; 4) 33.8; 5) 55.3.

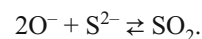
lated by introducing Na_2SO_4 , which is necessary to oxidize the excess sulfide sulfur.

It is evident that the presence of the reducer S^{2-} in slag glasses results in the appearance of the amber color (curve 1). In the color triangle they occupy the yellow part of the spectrum, close to orange, and possess adequate color purity but low color brightness, which explains the brown tint of the glasses. This tint intensifies, right up to a dark brown color, as more S^{2-} is introduced. Samples taken during different periods of the glass making process have shown that the color nonuniformity of the melt is high and the color becomes more uniform only at the mid-point of the glass-making stage. This can serve as one of the indirect characteristics of the process leading to the formation of coloring complexes taking account of the structural nonuniformity of the melt which forms.

The process responsible for the formation of an amber chromophore is quite complicated. When a high-temperature glass-forming melt forms a quite large number of active oxygen ions and a much smaller number of S^{2-} ions appear in it. The chemical oxygen affinity of Fe^{3+} ions is much higher than their sulfur affinity, and as a result Fe^{3+} complexes with oxygen ligands will form first. At the same time, under the action of high temperature and because the bonds formed are energy nonequivalent, partial dissociation of the oxygen complexes of Fe^{3+} occurs with a change of the coordination number and unstable reactive complexes $[\text{FeO}_4]^-$ form:

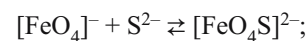


The presence of S^{2-} ions in the melt results in bonding of the oxygen ligands into SO_2 molecules:



Subsequently, the reaction proceeds by the following ligand substitution mechanism:

formation of an intermediate with a high coordination number:



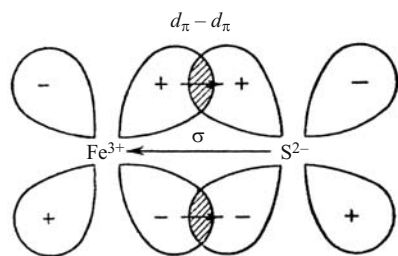
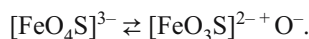
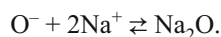
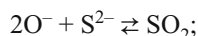


Fig. 4. Diagram of the formation of a $\text{Fe}^{3+} - \text{S}^{2-}$ π bond.

restructuring of the intermediate by “matched” transfer of ligands:



The detached oxygen ligands interact with the S^{2-} and Na^+ ions present in the melt, forming SO_2 molecules and cationic structural fragments:



When an amber chromophore forms, a S^{2-} ion, furnishing its p electrons for the formation of a σ bond with a Fe^{3+} ion, makes its own free d orbitals available for the formation of a π bond, in which the electrons are more mobile (Fig. 4). Ultimately, a stronger, double bond is formed, resulting in a distortion of the tetrahedral structure formed. The quite high intensity of the color is explained by the absorption of high-energy UV range, the nearby violet range of the visible spectrum, and the charge transfer effect. This imparts good photoprotective properties to glass used to make glass containers for storing food products, specifically, beer bottles.

For the curves presented in Fig. 3 it is necessary to take account of the difference between the transmission at 300 – 500 and 500 – 700 nm. For amber glasses (curve 1) this difference is quite large, and as the S^{2-} content decreases it too decreases and the color of the glass changes from yellow (curve 2) to light blue – green (curves 3 – 5). In the process, the Fe^{3+} coloring complexes are restructured from a tetrahedral structure with mixed ligands to an octahedral structure with oxygen ligands. Apparently, the change in the character of the transmission in the region 350 – 450 nm is due to not only a decrease of the concentration of S^{2-} ions but also the formation of an intermediate coordination structure with a change in the character of the bond between S^{2-} and Fe^{3+} . A transition occurs to a single bond between a sulfur ligand and the complex forming ion followed by “detachment” of the ligand, oxidation of the ligand, and a transition into a soluble state (SO_3).

The spectral transmission curves presented in Fig. 3 for glasses characterize the transition from “reduced” to “oxidized” glasses and vice versa. Taking into consideration the concepts of “reduced” and “oxidized” glasses [16] it should be noted that for the former the SO_3 content in the glass de-

creases because of the formation of SO_2 molecules and possible release of bubbles, while for the latter the SO_3 content in the glass increases. Consequently, the transition from one type of glass to another in a glass-making furnace should be made carefully in order to avoid a massive release of bubbles; a transition from “reduced” to “oxidized” glasses is more favorable.

In conclusion, it should be noted that the questions touched upon in this article concerning the formation of coloring complexes in glasses, including their interaction with the surrounding glass-forming medium, have not been adequately elaborated. This is also true for some structural features of glass-forming melts and the kinetic features of the processes occurring in them. Further elaboration of the tenets of the modern chemistry of coordination compounds using modern research methods could serve as one of the factors in the further elaboration of the scientific foundations of the technological processes that are used in glass manufacture.

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